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SYNTHESIS AND PROPERTIES OF SEVERAL NEW MOLECULAR CONDUCTORS. (U)

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <i>d superscript 8</i> Several d^8 metal complexes with columnar structures have been prepared using diaminoglyoxime, rubeanic acid, dithiooxalate, and dimethylglyoxime as ligands. These compounds are susceptible to partial oxidation using a variety of electron acceptors such as iodine and quinone. Upon oxidation, the electrical conductivities of these materials increase by as much as eleven orders of magnitude. The role of intermolecular association in the preparation of an excitonic superconductor is discussed.		

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"SYNTHESIS AND PROPERTIES OF SEVERAL NEW MOLECULAR CONDUCTORS"

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The preparation of highly-conducting materials which contain stacks or chains of coordinated metal ions continues to challenge synthetic chemists. As a synthetic aid, Keller (1) has developed guidelines for the preparation of such materials. These guidelines derive from both experimental observations and interpretations of the excitonic theory of superconductivity (2). This theory requires that a spine of delocalized charge carriers interacts via an excitonic mechanism with a proximal array of polarizable molecules (or ions) which will largely determine the exciton frequency. Although Little (3) has proposed several specific model compounds in which the essential features of the model might be realized, to date theoretical expectations are more nearly realized for the "organic metal" conductors than for the columnar transition-metal complexes. The latter materials possess a more-or-less conducting spine which is not strongly coupled (mechanically or electronically) to other molecules or ions in the lattice. Although this "insulation" of the conducting spine may lead to enhanced anisotropy in the electrical conductivity, it may also drastically lower the superconducting transition temperature of the material (by way of a Peierl's distortion or similar mechanisms.)

We are currently investigating the synthesis, electrical conductivity, and magnetic susceptibility of both single-valence and mixed-valence stacked complexes containing bifunctional ligands in order to ascertain the effect of weak interchain and/or donor-acceptor interactions. Our general synthetic outline is shown as two reactions in Fig. 1. In this figure M is a d^8 transition-metal ion capable of forming square-planar bis complexes with a bidentate ligand containing donor atoms L. Molecule (or atom) A

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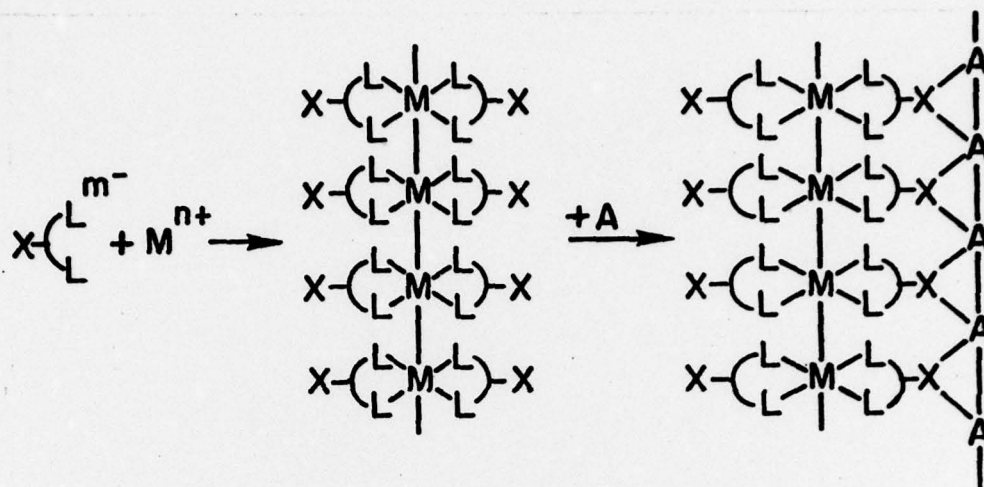


Fig. 1. General synthetic outline for coupled donor-acceptor stacks.

is an electron acceptor capable of partially oxidizing the metal chain. X is a functional group capable of hydrogen bonding to A . Acceptor A should be capable of crystallizing in stacks as well. Although we explicitly treat columnar structures with direct d^2 overlap, chain structures with ligand bridges are not excluded from consideration.

Several of the ligands we have used are illustrated in Fig. 2. Of these ligands, diaminoglyoxime and rubanic acid (dithiooxamide) are capable of forming very strong hydrogen bonds with chains of halide ions and chains of oxygen-containing electron acceptors. For this reason we have used the "classical" oxidizing agents Br_2 and I_2 as well as the unique oxidants p -quinone (1,4-benzoquinone, Q) and 1,4-naphthoquinone (NQ) (Fig. 2). Synthesis of the $Ni(II)$, $Pd(II)$, and $Pt(II)$ single-valence stacked complexes containing these ligands is normally carried out in aqueous solution although we often use ethanol-water mixed solvents to facilitate dissolution of the reactants. In some cases the crystals which are isolated from the reaction display striking color anisotropy.

We have obtained preliminary room-temperature electrical (dc) conductivity data (pressure contacts, 4-point probe) by using pressed pellets of these polycrystalline materials. Some typical results are given in Table I. This representative set of compounds contains anionic, neutral, and cationic chains with both nitrogen and sulfur donor atoms. The conductivities of these single-valence materials (Table I) are similar to the conductivities of related stacked d^8 complexes (weak semiconductors). It is interesting to note that although these complexes are all diamagnetic at

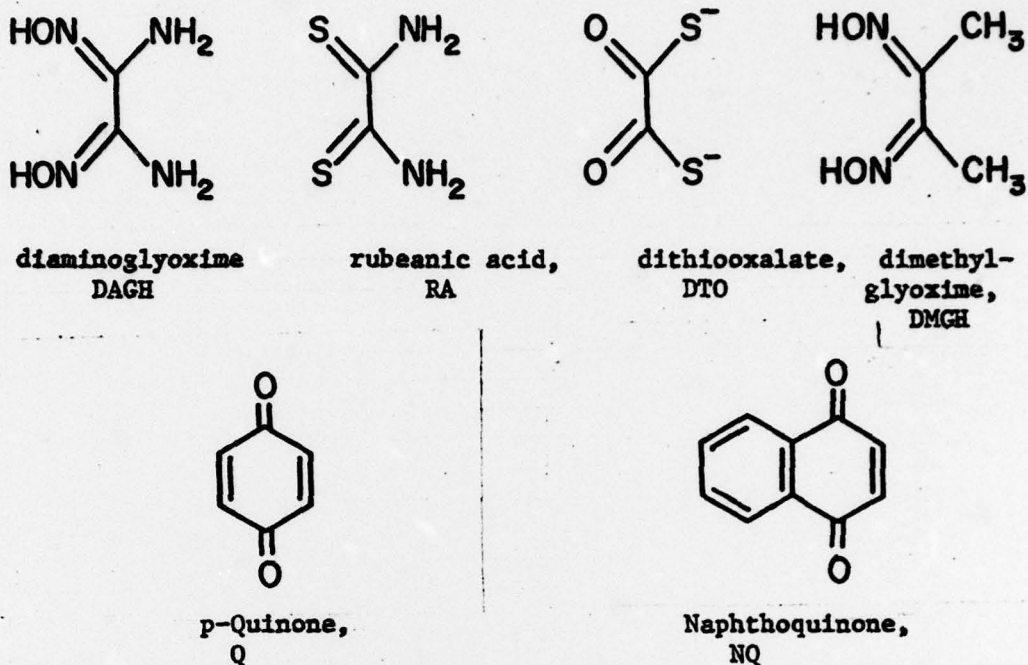


Fig. 2. Representative ligands and electron acceptors (quinones)

Table I. Single-Valence (Closed Shell) d^8 Complexes with Columnar Structures.

Complex	Color	$\sigma, 300K, \Omega^{-1} cm^{-1}$
Ni(DAG) ₂	red-yellow	3×10^{-8}
Pd(DAG) ₂	brown	1×10^{-7}
Pt(DAG) ₂	red-brown	2×10^{-8}
Ni(RA) ₂ Cl ₂	red-brown	5×10^{-10}
Pd(RA) ₂ Cl ₂	red	9×10^{-8}
Pt(RA) ₂ Cl ₂ ·xH ₂ O	red-violet	6×10^{-8}
K ₂ [Ni(DTO) ₂]	purple	1×10^{-9}
K ₂ [Pd(DTO) ₂]	red	8×10^{-8}
K ₂ [Pt(DTO) ₂]	violet	6×10^{-10}
Ni(DMG) ₂	red	5×10^{-11}
Pd(DMG) ₂	red	4×10^{-10}
Pt(DMG) ₂	violet	1×10^{-9}

300K (to within experimental uncertainty) they do possess a feeble Curie paramagnetism below ~ 200K. The origin of this paramagnetism may be due to monomeric impurities in the sample or may have its origin in other effects which are a reflection of the chain

structure of these materials.

We have used a variety of synthetic techniques for the preparation of mixed-valence analogs of the compounds in Table I. These techniques are best illustrated by considering specific examples. For example, Ni(DAG)_2 was treated with a stoichiometric amount of Br_2 in hot CH_3CN . To this solution was added a CH_3CN solution containing two equivalents of Ni(DAG)_2 . Upon cooling the resulting dark-yellow solution we obtain yellow-red crystals which analyze for $\text{Ni(DAG)}_2\text{Br}_{0.3}$. This partial oxidation technique has been previously utilized for the synthesis of KCP(Br) and is applicable for soluble starting materials.

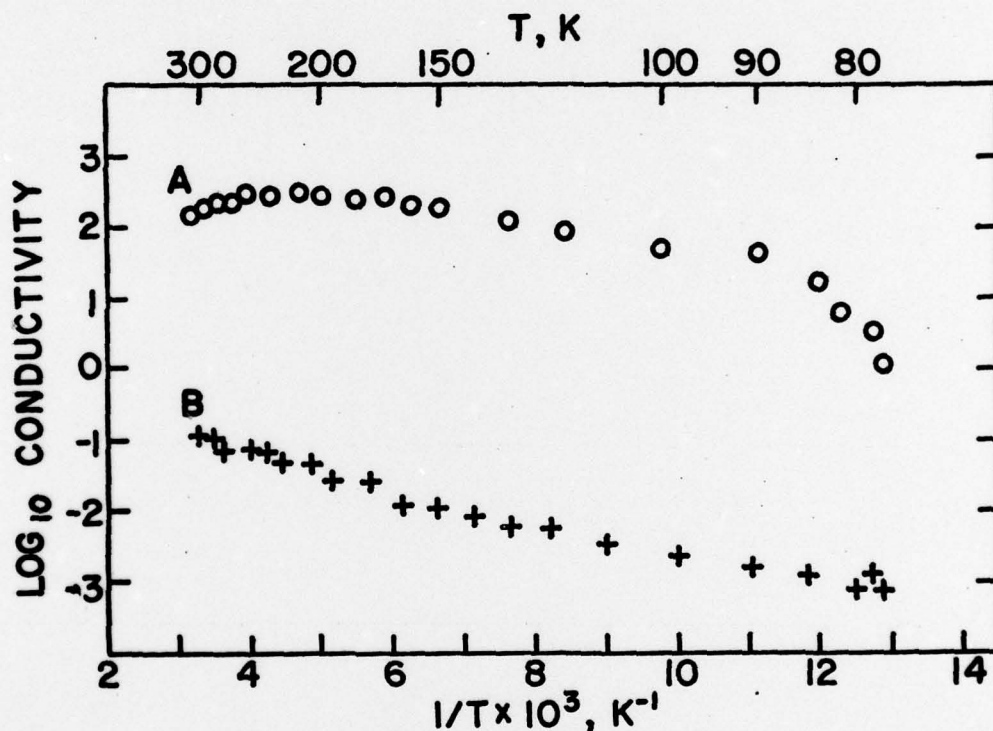
The iodine oxidation product of $\text{K}_2[\text{Ni(DTO)}_2]$ was obtained by a solid-state oxidation of the parent Ni(II) complex with a four-fold excess of I_2 at $90-100^\circ\text{C}$ in a sealed tube. Although this technique gives a well-defined product in this case, it suffers from the use of relatively high temperatures. For example, attempted oxidation of $\text{K}_2[\text{Pt(DTO)}_2]$ with I_2 in a sealed tube produces mainly PtS as the platinum-containing product.

We normally carry out oxidations with quinones by reacting a stoichiometric amount of quinone with the metal complex slurried in refluxing 1,2,4-trichlorobenzene (TCB). For example, treatment of 10 mmole of Ni(DMG)_2 with 10 mmole of p-quinone results in the formation of a dark violet product which contains one quinone unit per Ni(DMG)_2 , $\text{Ni(DMG)}_2\text{Q}$. We have also used TCB for I_2 and Br_2 oxidations of chain compounds.

Several materials obtained by these methods are listed in Table II. By comparing the pressed-pellet conductivities of these materials (Table II) with those of the parent d^8 complexes (Table I) an impressive increase in the room-temperature conductivity is evident in proceeding from the starting complex to its oxidation product. As an illustration, the conductivity of $\text{K}_2[\text{Ni(DTO)}_2]$ increases as much as eleven orders of magnitude upon iodine oxidation. We have thus far obtained several samples of this oxidation product which display metallic temperature dependence of conductivity in the approximate temperature range $200-300\text{K}$. Some typical pressed-pellet, four-probe dc conductivity data for $\text{K}_2[\text{Ni(DTO)}_2]\text{I}$ are shown in Fig. 3. The illustrated sets of points correspond to data obtained on two different preparations, A and B. Whereas samples A and B were prepared under apparently identical conditions, the former shows metallic conductivity in the temperature range $200-300\text{K}$ while the latter is a semiconductor in the entire temperature range studied.

Table II. Representative Oxidized Complexes.

Complex	Color	$\sigma, \Omega^{-1} \text{cm}^{-1}$ 300K^{-1}
$\text{Ni}(\text{DAG})_2\text{Br}_{0.3}$	yellow-red	4×10^{-5}
$\text{Ni}(\text{DAG})_2\text{Q}$	violet	9×10^{-2}
$\text{Ni}(\text{DAG})_2\text{I}$	red	9×10^{-3}
$\text{Pd}(\text{DAG})_2\text{Br}^x$	gold-brown	$6 \times 10^{-1} \text{ }^a$
$\text{Pt}(\text{DAG})_2\text{Br}^x$	gold-brown	$2 - 200 \text{ }^a$
$\text{Pt}(\text{RA})_2\text{Cl}_2\text{Br}_{0.3}$	yellow	8×10^{-2}
$\text{K}_2[\text{Ni}(\text{DTO})_2]\text{I}$	black	$0.5 - 200 \text{ }^a$
$\text{Ni}(\text{DMG})_2\text{I}$	violet	8×10^{-6}
$\text{Ni}(\text{DMG})_2\text{Q}^x$	violet	6×10^{-3}

^aSample dependent value.Fig. 3. Conductivity of two samples of $\text{K}_2[\text{Ni}(\text{DTO})_2]\text{I}$

(Sample A represents the most highly-conducting specimen of $\text{K}_2[\text{Ni}(\text{DTO})_2]\text{I}$ we have thus far prepared.) We have also measured the magnetic susceptibility of $\text{K}_2[\text{Ni}(\text{DTO})_2]\text{I}$ in the temperature range 20-300K. Both the metallic-conducting sample A and the

semiconducting sample B have room temperature magnetic moments near $1.73\mu_B$. Samples A and B both show Curie-Weiss behavior with $\theta = +26$ and $+12K$, respectively.

The bromine oxidation products of $Pd(DAG)_2$ and $Pt(DAG)_2$ also show high room-temperature conductivities (Table II). These materials are, however, semiconductors with activation energies of 0.15 and 0.06 eV, respectively. We have thus far been unable to isolate a sample of these oxidation products which displays metallic conductivity in the temperature range experimentally accessible to us. These materials lose Br_2 at room temperature - pressure and under vacuum. We have also noticed that passage of a current in excess of 1mV through these samples leads to enhanced loss of Br_2 . Room-temperature magnetic susceptibility data for these compounds indicate that they are diamagnetic materials.

The p-quinone oxidation products of $Ni(DAG)_2$ and $Ni(DMG)_2$ are both dark violet in color as compared to the yellow-red color of the $Ni(II)$ starting materials, and the oxidation products show a large enhancement in conductivity. Both $Ni(DMG)_2Q$ and $Ni(DAG)_2Q$ have room-temperature magnetic moments near $1.73\mu_B$ indicating one unpaired electron per Ni. Preliminary ESR spectra suggest that the electron is at least partly metal based.

Quinone oxidations of metal stacks are particularly interesting when discussed in light of the recent hypothesis of Perlstein (4) regarding the possible existence of an intermolecular migration of aromaticity in TCNQ-like salts. A tentative model for quinone oxidation products of stacked metal complexes is shown in Fig. 4. In this model the quinone stack is reminiscent of the structural role of TCNQ stacks in some organic metals. In order to confirm this proposed stacking arrangement of the quinone molecules it will be necessary to perform single-crystal X-ray studies on these materials. It has been our observation that a rather large number of columnar d^8 complexes may be oxidized by Q and NQ. Such oxidations may offer new synthetic routes to a different class of materials with high (possibly metallic) conductivities.

In conclusion we wish to briefly comment on a possible model of excitonic superconductivity based on mixed-valence stacked complexes containing bifunctional ligands and "polarizable" acceptor stacks. We will consider a stack of square-planar complexes bonded to I chains (Fig. 5a) and to p-quinone stacks (Fig. 5b). Whereas the electrical conductivity will still occur along the spine of metal ions, an excitonic mode will be enhanced by the interaction of the conduction electrons with the aromatic (charge) migration along the quinone-hydroquinone or iodine-iodide spine. The formation of electron pairs should be energetically favored by the nearest-neighbor polarization effects of the charged acceptor spine.

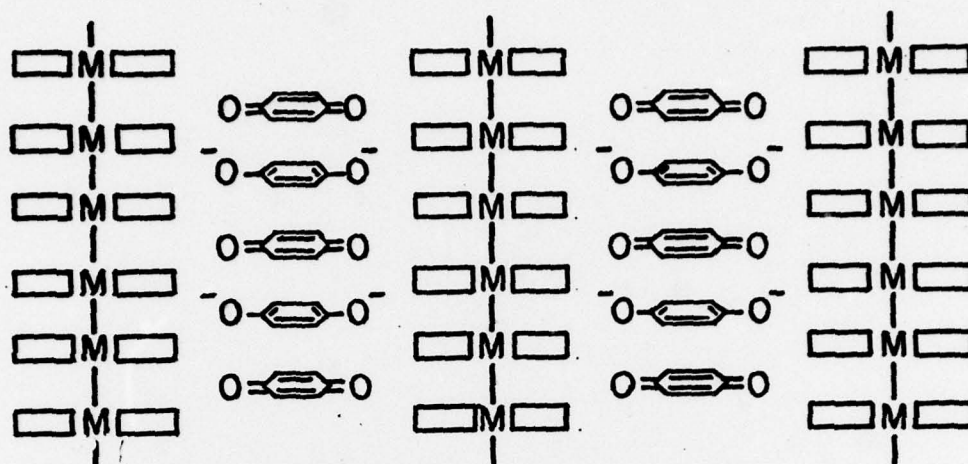


Fig. 4. Possible arrangement of oxidized metal stacks with intervening quinone-hydroquinone columns.

It seems probable that an interaction between acceptor and donor stacks will provide an opportunity for excitonic superconductivity. Unfortunately, very little experimental evidence to date is germane to this point. The series of oxidized compounds $\text{Ni}(\text{DMG})_2\text{I}$, $\text{Ni}(\text{DPG})_2\text{I}$ (5), $\text{Ni}(\text{BQD})_2\text{I}$, (6) and $\text{Ni}(\text{DAG})_2\text{I}$ shows a range of conductivities (8×10^{-6} , 1×10^{-7} , 2×10^{-5} , 9×10^{-3} , respectively) which may be explained by the model shown in Fig. 5a. However, great care must be exercised in attempting to make comparisons as all the compounds in this series do not contain equivalent Ni-Ni

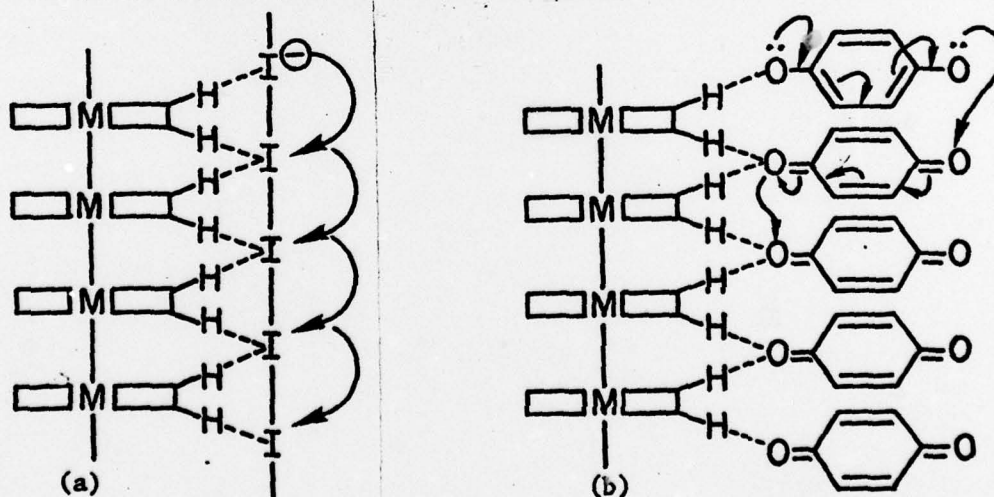


Fig. 5. Model of an excitonic superconductor with acceptor stacks of (a) iodine and (b) p-quinone.

separations or equivalent I sites. Future work on more diverse systems (particularly those capable of hydrogen bonding to the acceptor spine) should help to clarify these apparent trends.

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